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Encapsulated Lanthanides as Luminescent Materials

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Dedicated to Professor Roald Hoffmann on the occasion of his 65th birthday

Materials which embed organic dyes, rare earth ions, complexes, or quantum dots in a matrix with specifically tailored chemical and optical properties provide a challenging approach to novel chemical and optical applications. These materials have the potential to be used in microoptics, optoelectronics, laser materials, solar cells, sensors, battery electrodes, and photocatalysis. In this article we focus on lanthanides encapsulated in zeolites, glass films derived from sol – gel processes, and semiconductors.

The research work on the unique luminescent properties of rare earth elements hosted in different matrixes is strongly motivated by their technological importance in optoelectronic devices.[1] The materials emit over the entire spectral range of interest: near infrared (NIR; Nd^{3+}, Er^{3+}), red (Eu^{3+}, Pr^{3+}, Sm^{3+}), green (Er^{3+}, Tb^{3+}), and blue (Tm^{3+}, Ce^{3+}). Their optical transitions involve 4f orbitals, which are well shielded from their chemical environment by $5s^2$ and $5p^6$ electrons. The f-f transitions are parity forbidden and, as a result, the absorption coefficients are very low and the emissive rates are slow, which results in long-lived and linelike emission bands. As a consequence, direct excitation of the lanthanide ions is unfavorable. The comparatively fast thermal relaxation of the excitation energy is a problem when using lanthanide ions for luminescence. This nonradiative relaxation may occur by interaction of the electronic levels of the lanthanide ion with suitable vibrational modes of the environment.[2] The efficiency of these processes depends on the energy gap between the ground and excited states as well as the vibrational energy of the oscillators. For example, when solvents containing OH groups are coordinated to lanthanide ions, efficient nonradiative deactivations take place through vibronic coupling with the vibrational states of the OH oscillators. Replacement of the OH oscillators by low-frequency OD oscillators, diminishes the vibronic deactivation pathway.[3] Different ways to overcome the difficulties of low absorptivity and thermal relaxation have been used. We show the apparently most important ones in Figure 1: a) matrix excitation followed by energy transfer to the lanthanide ion, b) ligand →metal charge transfer followed by lanthanide f-f emission, and c) ligand-centered absorption followed by energy transfer to the lanthanide ion.

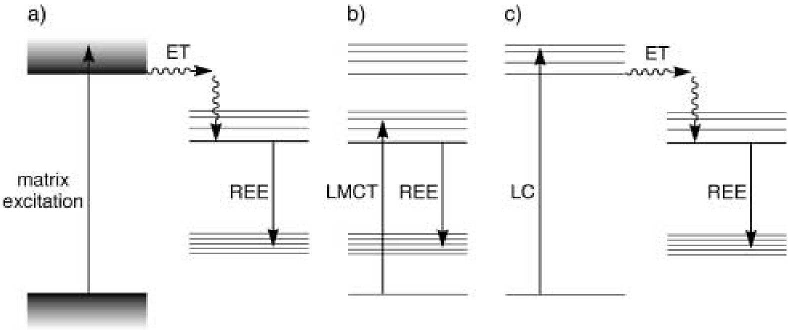

Figure 1. Three paths to efficient lanthanide luminescence (ET = energy transfer; REE = rare earth emission; LMCT = ligand →metal charge transfer absorption; LC = ligand-centered absorption). a) A matrix is excited above the band-gap energy and, after energy transfer, the lanthanide ion emits. b) Ligand →metal charge-transfer absorption can lead to an excited lanthanide ion which luminesces. c) Ligand-centered absorption excites a ligand which transfers its electronic excitation energy to a lanthanide ion that fluoresces.

We first discuss the use of coordinating ligands as sensitizers. After absorption of light by the ligands, the electronic excitation energy is transferred and results in a luminescence of the lanthanide ion (see Figure 1c). A possibility, given by Vögtle, Balzani, and co-workers, is to use a specially designed dendrimer which is able to play the role of the ligand for the lanthanide ions but which is also capable of working as an

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antenna.[4] The dendrimer was used as a light-harvesting ligand for enhancing the NIR luminescence of the Nd^{3+} ion.

Zeolites possess pore structures and these enable them to act as host for molecules and ions. The cations present in the pores of the zeolites have a charge-compensating function and can generally be exchanged. Rare earth ions and some of their complexes can be inserted by ion exchange.[5] Ligands can protect the lanthanide ions from the water molecules present in zeolites under ambient conditions.[2a] The zeolite framework itself, which consists of a corner-sharing network of tetrahedrally coordinated TO_4 units (T = Si, Al, P, Ga, B, Be, Ti), only has low vibration quanta which are not expected to contribute much to nonradiative deactivation of the excited state of the lanthanide ion. Ligands containing organic chromophores can be used to excite the lanthanide ion by the mechanisms shown in Figure 1 b and 1 c.[2a, 5b] However, conventional ligands do not usually give rise to inert complexes because the lanthanide ions are unable to form strong coordination complexes as a result of their electronic configuration.[2b] Depending on the solvent, this situation leads to a competition of the coordination sites between the ligands and solvent molecules. Lanthanide ions inside zeolite pores that are not complexed must be excited by sensitization of another species. For this, one can use, for example, Ce^{3+} ions which have allowed f-d transitions.[6] Intrazeolite transitions, which occur at about 180 nm in the UV spectrum, have been reported to sensitize lanthanide ions.[5a] It is not clear, however, to what extent charge-transfer transitions between the zeolite framework oxygen atoms and metal cations, which were found to be important in other cases, play a role in these materials.[7]

Another strategy is to use the high porositivity of glass films derived from sol–gel processes by incorporating inorganic lumophores, such as lanthanide cryptate or other macrocycles, as light-harvesting centers.[8] These efficiently collect photons and subsequently transfer their energy to the lanthanide ions to produce intense luminescence. The luminescence can be activated or enhanced by the presence of a molecule to be sensed. The target molecule must diffuse through the porous network of the film and bind to the lanthanide ion, thus increasing the emission of the light-harvesting centers. The sensors work by simply monitoring the emission intensity from the lanthanide centers. The advantageous mechanical and chemical stability, as well as the optical transparency of sol–gel matrixes, has been investigated as optical pH sensors based on luminescent lanthanide complexes.[9] Very recently, an enhanced fluorescence has been reported[10] from Eu^{3+}-doped silica gels in which CdS nanoparticles were adsorbed onto the pore surface of the gels. The CdS colloids were able to enhance the photoluminescence of the europium ions by energy transfer, even in the gel state.

Another way to minimize the difficulties of low absorptivity and nonradiative relaxation is by encapsulating the lanthanide ions in a semiconducting matrix. Charge carriers in a semiconductor can recombine at a lanthanide-related trap site in the matrix and transfer their recombination energy to the lanthanide ion, which then becomes excited and subsequently emits. Therefore, the lanthanides have been studied as emission amplifiers for semiconductors, which have an intrinsic indirect bandgap, such as silicon.[11] Er^{3+}-doped silicon nanoparticles have been prepared by copyrolysis of disilane and a volatile erbium complex. These materials show a characteristic NIR photoluminescence of the Er^{3+} ion at 1540 nm.[12] The charge carriers can be generated optically, which results in photoluminescence, or electrically, which gives electroluminescence. Both processes have been observed at room temperature in Eu^{3+}-doped thin films of GaN grown on Si substrates.[13] Conde-Gallardo et al. showed that the semiconducting nature of TiO_2 grown by the sol–gel method on glass and on a crystalline silicon substrate provides a suitable environment for enhancing the luminescence of the Eu^{3+} ion.[14] Excitation above the bandgap energy of the $Eu^{3+}–TiO_2$ layers on glass or on silicon lead to intense Eu^{3+} emission. The process seems to correspond to the mechanism shown in Figure 1 a. Excitation below the bandgap energy mainly caused some weak luminescence from a TiO_2 defect.

Thermally stable and ordered mesoporous metal oxides (for example, TiO_2, ZrO_2, Al_2O_3, $SiTiO_4$, $ZrTiO_4$) are interesting and attractive host matrixes. Stucky and coworkers reported a simple and versatile synthesis for materials with a pore size of up to 14 nm.[15] They used amphiphilic block copolymers as structure-directing agents in non-aqueous solutions. Hexagonal or cubic mesostructures have been obtained, depending on the agent used. These mesoporous oxides contain nanocrystalline domains within relatively thick amorphous walls. For example, a well-ordered cubic array of TiO_2 mesopores of about 7–8 nm in size and a wall structure composed of 1–5-nm anatase nanocrystallites embedded in an amorphous titanium oxide matrix was obtained by this procedure.[16] This interesting two-phase wall structure of ordered TiO_2 nanoparticles was successfully tested as a host for Eu^{3+} ions.[17] A cubic mesostructured matrix of titanium dioxide with a three-dimensional array of embedded anatase nanocrystals was doped with high concentrations of Eu^{3+} ions (up to 8 mol%). The semiconducting anatase nanocrystallites were found to sensitize the Eu^{3+} activator, which leads to an energy-transfer system shown in Figure 1 a) that produces a bright red luminescence (ca. 614 nm). Most amazing is the simple preparation by dip-coating and subsequent heat treatment of such films. These films were reported to have a self-assembled framework, high surface area, and to be air and moisture stable.

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